

We therefore claim:

1. A method of making a catalyst for the production of hydrogen, said catalyst comprising from about 60 wt% to about 95 wt% Fe<sub>2</sub>O<sub>3</sub>, from about 0 wt% to about 20 wt% Cr<sub>2</sub>O<sub>3</sub>,  
5 and from about 0 wt% to about 10 wt% CuO, and said method comprising:
  - a) preparing an aqueous organic acid solution, wherein said organic acid is a carboxylic acid having at least one carboxylic acid group with a pK<sub>a</sub> at ambient temperature of from about 0.5 to about 6;
  - b) adding iron metal to said acid solution;
  - 10 c) forcing an oxidative agent through said acid solution until said iron metal is consumed and an iron slurry is formed;
  - d) milling said iron slurry to a particle size with a D<sub>50</sub> of less than about 2 microns;
  - e) adding at least one promoter to said milled iron slurry to form a product slurry, said promoter being added at a concentration such that said product slurry has a solids content of from about 10 % to about 40 % inclusive of said promoter;  
15 f) drying said slurry to form particles;
  - g) mixing in chromic acid flakes; and
  - g) calcining said particles to form said catalyst.
- 20 2. The method of Claim 1 wherein said organic acid is selected from the group consisting of formic acid, acetic acid, glycolic acid, oxalic acid, pyruvic acid, malonic acid and propionic acid, and a combination thereof.
- 25 3. The method of Claim 1 wherein said iron metal is a powder, granule, sphere, chip or other form having an average diameter of from about 1μ to about 500μ.

4. The method of Claim 1 wherein said promoter is selected from the group consisting of cerium, chromium, iridium, lanthanum, manganese, molybdenum, palladium, platinum, rhenium, rhodium, ruthenium, strontium, tungsten, vanadium, zinc, potassium oxide, rubidium oxide, cesium oxide, magnesium oxide, titanium oxide, zirconium oxide, aluminum oxide, silica, scandium, yttrium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, other rare earth metals and combinations thereof.

5 5. The method of Claim 1 wherein said slurry is spray dried with a wheel atomizer.

10 6. The method of Claim 1 wherein said catalyst comprises from about 80 wt % to about 95 wt % iron oxide.

7. The method of Claim 1 wherein said catalyst has an essentially spherical particle shape and relatively small particle size distribution range.

15 8. The method of Claim 1 wherein said oxidizing agent is air, compressed air, oxygen, hydrogen peroxide, an organic peroxide, ozone and a combination thereof.

9. The method of Claim 1 wherein said catalyst further comprises from about 0 wt% to 20 about 10 wt% of a component selected from the group consisting of ZrO<sub>2</sub>, TiO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and CeO<sub>2</sub>.

10. A method of making a catalyst for the production of hydrogen, said catalyst comprising from about 60 wt% to about 95 wt% Fe<sub>2</sub>O<sub>3</sub>, from about 0 wt% to about 20 wt% Cr<sub>2</sub>O<sub>3</sub>, 25 and from about 0 wt% to about 10 wt% CuO, and said method comprising:

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- a) preparing an aqueous organic acid solution, wherein said organic acid is a carboxylic acid having at least one carboxylic acid group with a pK<sub>a</sub> at ambient temperature of from about 0.5 to about 6;
  - b) adding an iron source to said acid solution, wherein said iron source is an iron metal powder, granule, sphere, chip or other form having an average diameter of from about 1μ to about 500μ;
  - c) forcing an oxidative agent through said acid solution until said iron source is consumed and an iron slurry is formed;
  - d) milling said iron slurry to a particle size with a D50 of less than about 2 microns;
  - 10 e) adding at least one promoter to said milled iron slurry to form a product slurry, said promoter being added at a concentration such that said product slurry has a solids content of from about 10 % to about 40 % inclusive of said promoter;
  - f) drying said slurry to form particles;
  - 15 g) mixing in chromic acid flakes; and
  - h) calcining said particles to form said catalyst.
11. The method of Claim 10 wherein said milled slurry is spray dried with a wheel atomizer.
- 20 12. The method of Claim 10 wherein said iron slurry has a solids content of from about 10 % to about 40 %.
13. The method of Claim 10 wherein said organic acid solution is prepared from water and an acid selected from the group consisting of formic acid, acetic acid, glycolic acid, oxalic acid, 25 pyruvic acid, malonic acid and propionic acid, and a combination thereof.

14. The method of Claim 10 wherein said oxidizing agent is air, compressed air, oxygen, hydrogen peroxide, an organic peroxide, ozone and a combination thereof.

15. The method of Claim 10 wherein said promoter is selected from the group consisting of cerium, chromium, iridium, lanthanum, manganese, molybdenum, palladium, platinum, rhenium, rhodium, ruthenium, strontium, tungsten, vanadium, zinc, potassium oxide, rubidium oxide, cesium oxide, magnesium oxide, titanium oxide, zirconium oxide, aluminum oxide, silica, scandium, yttrium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, other rare earth metals and combinations thereof.

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16. The method of Claim 10 wherein said catalyst further comprises from about 0 wt% to about 10 wt% of a component selected from the group consisting of  $ZrO_2$ ,  $TiO_2$ ,  $Co_3O_4$ ,  $Al_2O_3$ ,  $SiO_2$  and  $CeO_2$ .

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17. A catalyst for the production of hydrogen, said catalyst being prepared by reacting an essentially contaminant-free iron source with an organic acid and air to form an iron oxide slurry, adding one or more promoters to said iron oxide slurry to form a promoter slurry, spray drying said promoter slurry, adding a chromium source to form a product mix, and calcining said product mix, and wherein said catalyst comprises from about 60 wt% to about 95 wt%  $Fe_2O_3$ , from about 0 wt% to about 20 wt%  $Cr_2O_3$ , and from about 0 wt% to about 10 wt%  $CuO$ .

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18. The catalyst of Claim 17 wherein said catalyst further comprises from about 0 wt% to about 10 wt% of a component selected from the group consisting of  $ZrO_2$ ,  $TiO_2$ ,  $Co_3O_4$ ,  $Al_2O_3$ ,  $SiO_2$  and  $CeO_2$ .

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19. The catalyst of Claim 17 wherein said essentially contaminant-free iron slurry is prepared by reacting an iron source selected from an iron metal powder, a granule, a sphere, a chip or a particle having an average diameter of from about 1 $\mu$  to about 500 $\mu$ , with an aqueous organic acid solution and an oxidizing agent.

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20. The catalyst of Claim 17 wherein said organic acid solution is prepared from water and a carboxylic acid having at least one carboxylic acid group with a pK<sub>a</sub> at ambient temperature of from about 0.5 to about 6, and said oxidizing agent is air, compressed air, oxygen, hydrogen peroxide, an organic peroxide, ozone and a combination thereof.

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21. The catalyst of Claim 17 wherein said promoter is selected from the group consisting of cerium, chromium, iridium, lanthanum, manganese, molybdenum, palladium, platinum, rhenium, rhodium, ruthenium, strontium, tungsten, vanadium, zinc, potassium oxide, rubidium oxide, cesium oxide, magnesium oxide, titanium oxide, zirconium oxide, aluminum oxide, silica, scandium, yttrium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, other rare earth metals and combinations thereof.